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TARRYTOWN NY C L SCHILLING SEP 83 TR-83-4
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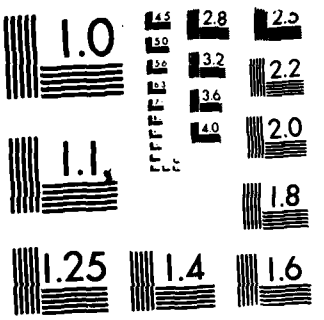

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Copolymers	Ceramics

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Preparation, properties, and conclusions regarding organosilane polymers and their conversion to silicon carbide ceramics during the contract period are summarized. The polymers include high molecular weight polydimethylsilanes, alkyl-modified, soluble polydimethylsilanes, polysilane block copolymers, polysilahydrocarbons, and vinylic polysilanes.

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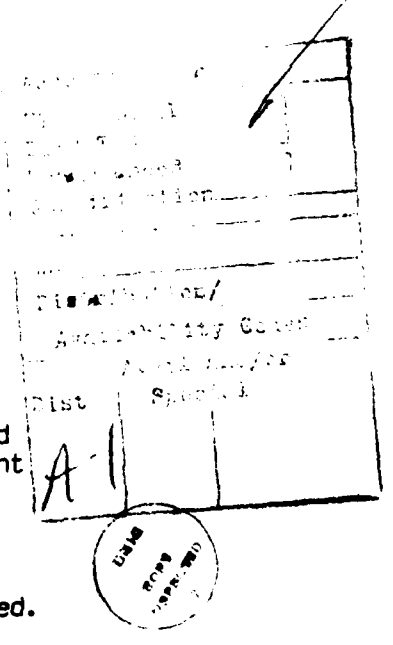
ORGANOSILANE POLYMERS, VIII:

FINAL REPORT

by

C. L. Schilling Jr.

Union Carbide Corporation
Tarrytown, New York 10591



September 1983

ORGANOSILANE POLYMERS, VIII:

FINAL REPORT

INTRODUCTION

This report summarizes research results from the title program, which began under Contract N-00014-75-C-1024 (6.1 partial funding, 1 May 1975 to 31 March 1981) and continued under Contract N-00014-81-C-0682 (6.2 funding, 1 April 1981 to 30 July 1983).

Research began as a fundamental study of polydimethylsilanes, and led to improvement of their solubility properties by modification with other alkyl groups. Polysilane block copolymers followed, having improved solubility as well as film-forming properties. The successful conversion (by Japanese researchers) of polydimethylsilanes to preceramic polymers and ultimately to silicon carbide (SiC) ceramic compositions, including fibers, prompted attempts at converting polymers from this program to ceramics. The study of vinylmethyldichlorosilane (CH_2=CHSiMeCl_2) as a monomer culminated in the preparation of a variety of useful organosilicon polymeric precursors for SiC, in the fundamental understanding of the structural features necessary for effective conversion of these polymers to ceramics, and in the observation of fundamental differences in the reactivities of the active metals used to prepare these polymers.

Program Achievements

A consistently high level of success has been achieved during this program, as demonstrated by the following accomplishments.

High molecular weight polydimethylsilanes were prepared by dechlorination of highly purified dimethyldichlorosilane (Me_2SiCl_2) with sodium (Na) or sodium/potassium (Na/K) alloy.[1] These polymers were largely crystalline, high melting, and sparingly soluble, even above 200°C in high boiling solvents.

Solubility properties were greatly improved via polymers prepared from Na dichlorination of mixtures of Me_2SiCl_2 with either ethylmethyldichlorosilane (EtMeSiCl_2) or propylmethyldichlorosilane (PrMeSiCl_2).[2] The products are copolymers wherein ethyl or propyl groups in effect replace a portion of the methyl groups.

Improved solubilities were also obtained in block copolymers prepared from well-defined chloro- and lithio-terminated oligomeric polysilanes.[3] These materials showed coherent film-forming abilities (as cast from solutions) not observed in earlier candidates.

One-step preparations of tractable polycarbosilanes were achieved through silicon-carbon bond-forming reactions of mixtures of vinylic or chloromethyl ($ClCH_2Si$≡) silanes with other chlorosilanes.[4,5] The reactions occurred during K metal dechlorinations of such mixtures, providing polymers which were directly convertible to SiC ceramic compositions by unconfined pyrolysis. Backbone branching at silicon atoms was recognized as essential for practical conversion of such polymers to SiC.

The isolation of silylated tetrahydrofuran (THF) derivatives from certain K/THF dechlorinations provided evidence for THF side reactions previously unobserved in active metal/chlorosilane chemistry.[6]

The incorporation of hydrosilyl (≡SiH) groups into the above polycarbosilanes by use of methyldichlorosilane ($MeSiHCl_2$) as a monomer provided improved ceramic yields.[7,8] Polycarbosilanes with and without ≡SiH groups were successfully spun to preceramic fibers through a subcontracted effort at Albany International Research Company.

The importance of backbone branching at silicon atoms in providing good ceramic yields was confirmed by preparing branched polysilahydrocarbons via K dechlorination of chlorosilanes in the presence of hydrocarbon olefins, such as styrene or isoprene.[9,10] The use of $MeSiHCl_2$ again provided polymers with improved ceramic yields, with a copolymer derived from $MeSiHCl_2$/isoprene performing well in ceramic screening at the Naval Research Laboratories.

The use of Na metal, specifically in certain solvent blends, as a dechlorinating agent for mixtures of CH_2=CHSiMeCl_2 with other chlorosilanes, provided vinylic polysilanes which were excellent ceramic precursors.[11,12] The vinyl groups provide a means of non-oxidative curing or crosslinking, an effect which is also enhanced by ≡SiH groups, and which is a major advantage in preceramic processing. Very promising results have been achieved at NRL[13] with vinylic polysilanes in ceramic matrix testing.

Program Conclusions

The above achievements have led to the following conclusions:

- High molecular weight polydimethylsilanes can be prepared, but are not useful in terms of currently desired physical properties.
- Solubility properties are improved by replacing a portion of the methyl groups with larger hydrocarbon groups, such as ethyl or propyl groups, or by preparing block copolymers.
- Block copolymers consisting of dimethylsilyl or diethylsilyl oligomeric blocks, and diphenylsilyl oligomeric blocks, show film-forming capabilities, as well as improved solubilities.
- Potassium-derived polycarbosilanes are effective precursors for silicon carbide ceramic compositions, with backbone branching at silicon atoms being an essential structural feature.
- Tetrahydrofuran is not a totally inert solvent in potassium dechlorinations, and provides low yields of ring-intact silylated derivatives.
- Branched polysilahydrocarbons, derived from chlorosilanes and hydrocarbon olefins such as styrene or isoprene by potassium dechlorination, are also effective SiC ceramic precursors.

- Vinylic polysilanes, which form backbone branches at silicon atoms via thermal crosslinking, are very effective SiC ceramic precursors.
- Hydrosilyl modification of polycarbosilanes, polysilahydrocarbons, and vinylic polysilanes provides polymers with enhanced ceramic yields.

Program Participants

Supervisors

Thomas C. Williams - 1 May 1975 - 31 December 1980.
Bernard Kanner - 1 January 1981 - 30 July 1983.

Principal Investigators

John P. Wesson - 1 May 1975 - 31 August 1979.
Curtis L. Schilling, Jr. - 1 September 1979 - 30 July 1983.

Laboratory Assistants

Timothy Donohue - 1977-78 - Irregular.
Deborah Williams - 1 November 1980 - 28 February 1982.
Juan Alfonso - 1 January 1982 - 30 July 1983.

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12. U.S. Patent Application, Serial No. 480,700 filed March 31, 1983.

13. Ceramic screening tests were performed in Ceramics Branch, Naval Research Laboratories, under Dr. Roy Rice.

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